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The First Deslandres' Group of the Positive Band Spectrum of Nitrogen, under High Dispersion

A THESIS
SUBMITTED FOR THE DEGREE OF DOCTOR
OF PHILOSOPHY

BY

RAYMOND T. BIRGE

UNIVERSITY OF WISCONSIN
PH. D. THESIS 1914

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1913

[illegible]

THE FIRST DESLANDRES' GROUP OF THE
BAND SPECTRUM OF NITROGEN, UNDE
DISPERSION

BY RAYMOND T. BIRGE

This paper is a preliminary discussion of the Firs
Group of the band spectrum of nitrogen, based mainly
graphs taken by the author in the second order
concave grating, from λ5000 to λ6800. The banc
completely resolved into lines and the discussion in
concerned with the relations between the lines form
principal heads of the bands.

INTRODUCTION

The positive band spectrum of nitrogen has bee
of a large number of investigations. Under low
apparent regularity of the bands, both in position a
ances is very striking. The violet end of this spectr
be photographed under high dispersion, but becaus
tively low intensity in the longer wave-lengths, th
not previously been resolved into its component li
factory manner. Von der Helm¹ made the latest
two objects of his investigation, with his success in
them, are stated as follows:

1. [illegible]
[illegible]
2. [illegible]
[illegible]
[illegible]

Von der Helm gives a complete discussion of rel
work on nitrogen, together with the possible resu
investigation, and the first eight pages of his art
as an introduction to this paper.

The First Deslandres' Group of bands extend
[illegible] Measurements on the band

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¹ [illegible]

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bands have previously been made to λ 9100. The results seem to show that the spectrum consists of a series of band groups, each of which is most intense at the center, and diminishes in intensity toward either side. Kayser's *Handbuch*[1] gives only three groups, which he calls *a*, *b*, and *c*. Other groups of longer wave-length have since been found, and it appears now that there are six groups in all, which will be designated *a* to *f* respectively.

Group *a* 1.06 μ (?)
Group *b* 9101 (?) to 7887
Group *c* 7887 to 7059
Group *d* 7059 to 6185 (Kayser's *a* group)
Group *e* 6186 to 5485 (Kayser's *b* group)
Group *f* 5632 to 5126 (Kayser's *c* group)

Group *f* is quite different from the others. It has two intensity maxima, one at λ 5200 and the other at λ 5475. This would indicate two groups, but as the spacing is the same in both, it has been customary to classify them together. This group also overlaps considerably on group *e*.

The author obtained, besides the exposures on the large grating, one on a Hilger constant deviation spectroscope, extending to λ 7650. From this point to λ 9100 we have only the measurements of Croze.[2] Coblentz,[3] in connection with other infra-red work, has recorded positions of maximum intensity at 0.546, 0.667, 0.75, 0.90, and 1.06 μ. These are very evidently the approximate positions of maximum intensity in the several band groups. The reading at 1.06 μ points to the existence at this point of another group, which we have called group *a*.

In making this investigation the author had two objects in view: (1) to determine whether or not the bands in any one group were identical; (2) to determine, in case there were any similarities, whether corresponding lines in successive bands would fit into a Deslandres' series or other arithmetical relation.

The results of the study made thus far indicate that out of the 250 or more lines composing each band, at least 50 of the strongest are related to corresponding lines in other bands, and that the relationship is approximately that expressed by Deslandres' Law:

$$v=a+b(m+c)^2$$

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[1] *Handbuch der Spectroscopie*, **5**, 828.

[2] *Comptes rendus*, **150**, 860, 1910.

[3] *Physical Review*, **22**, 1, 1906.

where a, b, and c are constants, and m takes successive integral values.

EXPERIMENTAL ARRANGEMENTS

Atmospheric nitrogen, free from oxygen, carbon dioxide, and water-vapor, was used as a source. Hence the inert gases of the atmosphere were present, but the only lines due to them which have thus far been noted are a few of the stronger argon lines of the red spectrum. There is no trace of helium λ 5876. Traces of mercury diffused into the spectrum tube from the pressure gauge, but only the three strong lines at λ 5790, λ 5769, and λ 5461 appear, the last enormously overexposed.

The nitrogen was electrically excited in a Goetze "Type C" spectrum tube. The emission from the capillary of such a tube, in a "head-on" direction, appears to be the most intense, per unit cross-section, now obtainable. The electrical excitation was furnished by the secondary of a large induction coil, the primary being run on 110 volts A.C., 1.5 amperes. The nitrogen was introduced at about 5 mm pressure and used until the pressure fell to about 1 mm, low enough to cause a slight diminution of the radiation. Refilling of the tube was necessary only once in 24 to 36 hours.

The tube was placed accurately "head-on" to the slit of the grating, 60 cm away. A double convex lens of 15 cm focus produced on the slit a sharp image of the end of the capillary, somewhat more than 1 mm in diameter. This usual arrangement was now varied by introducing, at a distance of 12 cm from the slit, a double concave cylindric lens of 12 cm focus, placed with its axis horizontal. This caused the circular image on the slit to be drawn out into a vertical line some 2 cm in length. The use of such a cylindric lens in spectrum work has been advocated by Humphreys,[1] but I know of no definite statement of the advantages and disadvantages incident to its use.

The action of the cylindric lens is greatly to reduce the vertical aperture of the cone of rays proceeding from the slit. With the particular lenses used, it is possible, with a source of light less than approximately 2 mm in diameter, to reduce the vertical aperture, at the grating, to less than the length of the grating rulings. Thus the cross-section of the cone of light at the grating, instead of being a 75-cm circle, is reduced (roughly) to an ellipse of 75 cm horizontal diameter, but with a vertical diameter of 5 cm or less. The gain in intensity of the middle point of the astigmatic image at the camera is theoretically $\frac{75\text{ cm}}{5\text{ cm}}=15$. The actual increase, determined experimentally, was thirteen fold.

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[1] *Astrophysical Journal*, 18, 324, 1903.

If now the source is made 4 mm in diameter, instead of 2, the amount of light actually striking the grating, using the cylindric lens, is scarcely increased at all. But with the ordinary arrangement, the amount would practically be doubled. Hence the advantage of the cylindric lens is proportionally decreased. For sources more than 2 cm in diameter, there is no appreciable advantage in using a cylindric lens.

The chief disadvantage attendant upon its use is the necessity of accurate adjustment. The centers of the tube, convex lens, concave lens, and slit should all lie accurately in the horizontal plane formed by the center of the grating and of the camera. With this condition fulfilled, and the cone of light falling symmetrically upon the grating, a raising or lowering of the cylindric lens of even one-tenth of a millimeter is sufficient to throw an appreciable portion of the light entirely below or above the rulings of the grating.

Because of the excess of radiation in a "head-on" direction, the illumination of the grating is far from uniform; but this is true even when the cylindric lens is not used. Such a non-uniformity is liable, however, to cause a shift of the lines of the comparison spectrum relative to those under investigation. The actual shifts found in many cases, between the iron and nitrogen lines, are believed to be due primarily to this cause.

As a comparison source I used an iron arc of the Pfund[1] type, run on 200 volts, 5 amperes, with iron and carbon electrodes. It worked in a very satisfactory manner. The exposures were made in the second order, and both the second-order and coincident third-order international iron normals were used, the measurements in the ultra-violet being those of Buisson and Fabry,[2] not yet officially adopted as standards.

No relative shift of orders could be detected on those plates where both the second- and third-order normals were present.

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[1] *Astrophysical Journal*, 27, 296, 1908.

[2] *Ibid.*, 28, 169, 1908.

Whenever two normals fell near together and were both of suitable intensity for an accurate setting, the agreement was perfect. When one or both lines were overexposed the disagreement might be anything from 0.007 A down. This was taken to indicate that the secondary international normals, when overexposed, do not necessarily broaden symmetrically. The much greater uniformity in intensity of the normals between λ 3500 and λ 4500 thus makes them preferable for use, and this fact, coupled with the great faintness of the normals from λ 5900 into the red, caused the author to use only the coincident third-order normals in the region λ 5900 to λ 6800.

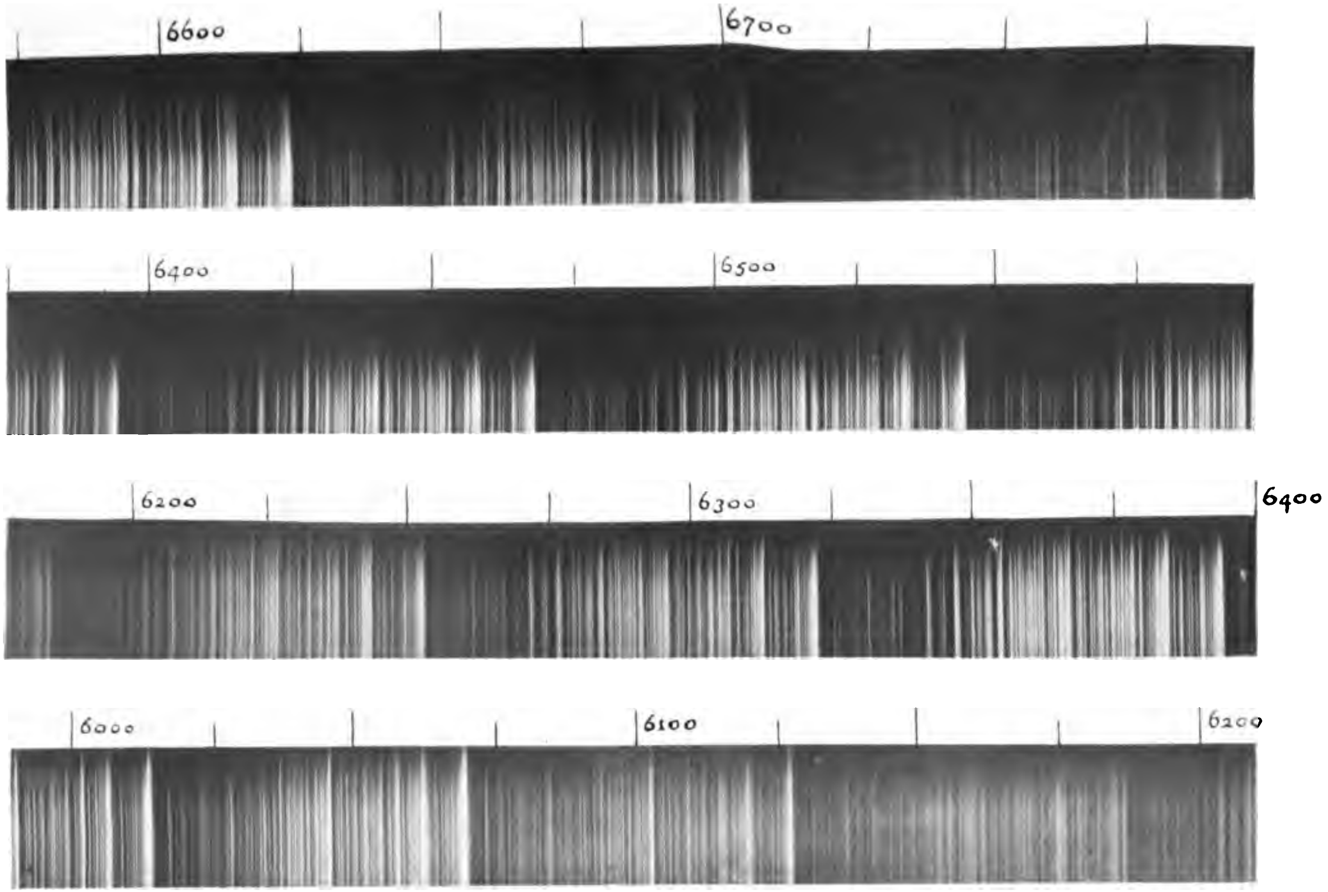
In order to eliminate the exceedingly strong violet bands of nitrogen, an 8 per cent solution of potassium chromate 5 mm thick was employed. The absorption of this solution sets in at about λ 5200 and this accounts for the rapid decrease in intensity below this point. (See Plate III.) Although the head of the λ 3576 band is a thousand times as intense, photographically, as that of any band under investigation, no trace of it appears on the exposures. Fluorescein was tried as an absorbent and found quite ineffective.

For the exposures from λ 5000 to λ 5900 the Cramer Instantaneous Isochromatic plates were employed, while from λ 5800 to λ 6900 both Cramer "Spectrum" and Wratten & Wainwright "A" Panchromatic were used. For the one exposure on the Hilger spectroscope, from λ 6800 to λ 7700, I used a Wratten & Wainwright "B" Panchromatic plate.

The strongest portion of the spectrum, from the photographic standpoint, is that from λ 5700 to λ 5800. The λ 5804 band is fully three times as intense as that at λ 6623, the only one which von der Helm appears to have obtained sufficiently intense for measurement. The region from λ 5500 to λ 5900 was accordingly photographed first, using 12×1¼ inch plates, and the usual Rowland type of comparison shutter. All other exposures were made with 18×2½ inch plates, using a comparison shutter, mounted independent of the camera.

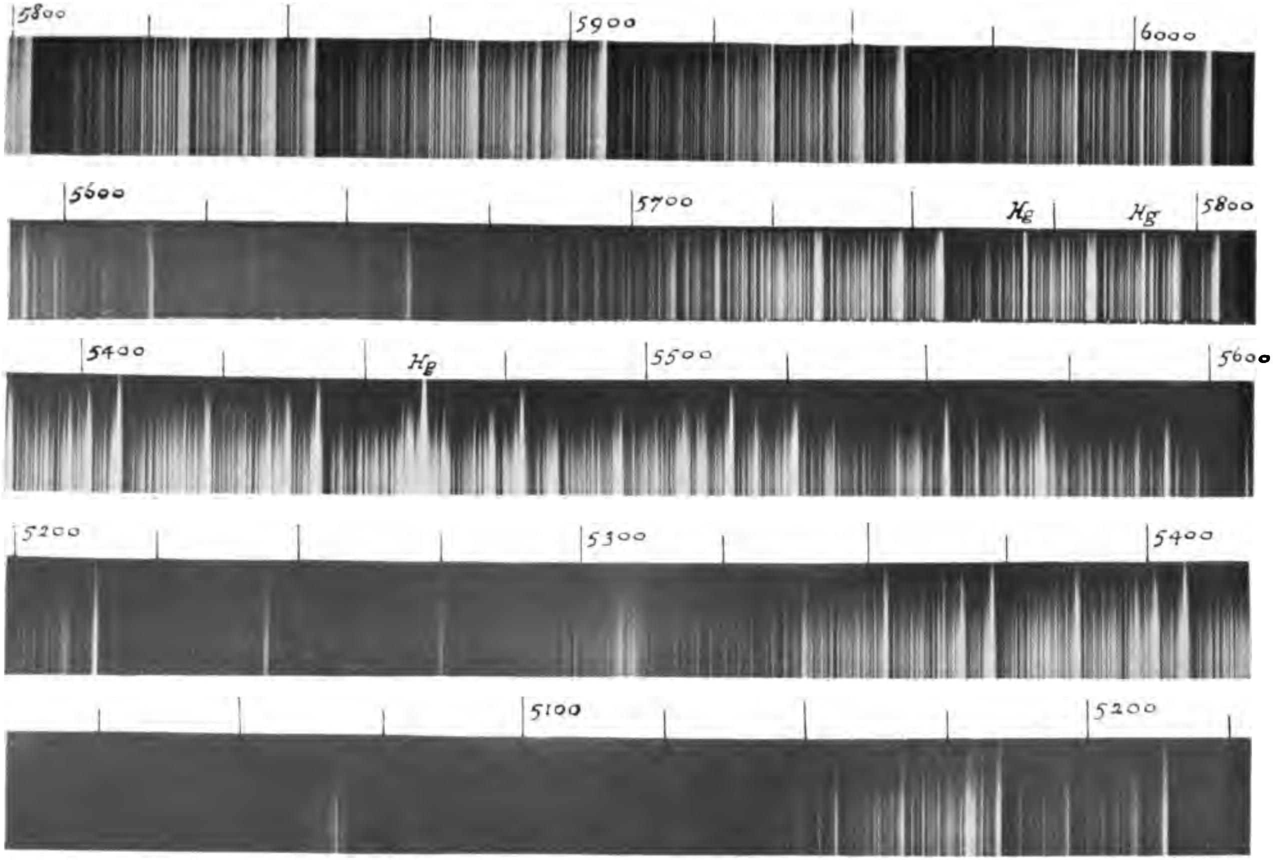
In making exposures several days in length, the greatest problem is a proper control of temperature. Fortunately for the author, the large grating of the University of Wisconsin is mounted inside a double-walled room, built in turn entirely inside an ordinary room.

PLATE II



Positive Band Spectrum of Nitrogen

PLATE III



Positive Band Spectrum of Nitrogen

The temperature in this outer room was kept constant within a few tenths of a degree by suitable electrical heating. This enabled the temperature of the grating to be kept constant within a few hundredths of a degree. The grating temperature was read on an accurate mercury thermometer, mounted in metallic contact with the side of the grating. Other thermometers were laid in a slot in the iron beams forming the slit-grating-camera triangle. A small change of temperature in this triangle is immaterial, so long as all parts remain at an equal temperature.

For the grating, however, a constant temperature is indispensable, the change of wave-length at a given point on the camera plate being proportional, to first-order effects, to the change in the width of the grating space.[1] Holtz[2] seems to question this, and spends some time searching for other causes for the observed shift of lines with temperature. The mounting of the grating at the University of Wisconsin is such as to exclude the chief sources of error which he mentions, and it was found experimentally that the shift was exactly that computed from the change of temperature and the coefficient of expansion of the grating.

A change of 0°01 C. in the grating temperature will shift a line (at λ 5000) about 0.001 A. During the exposures the temperature was never allowed to leave a 0°1 C. range, and during any one exposure the average variation from the mean temperature varied, in different exposures, from 0°015 to 0°035 C. The broadening of the lines was thus always less than 0.01 A.

Not only the temperature, but the barometric pressure as well, causes a shift of the spectrum. A change of 1 mm in pressure will shift the lines 0.002 A. With frequent total pressure variations of 2 cm, sufficient to cause a 0.04 A broadening of the lines, it becomes necessary to eliminate this change also. This was done by arbitrarily changing the temperature. A 1 cm rise of pressure is compensated by a 0°15 lowering of temperature. The mean temperature mentioned above, which I endeavored to hold constant, refers to the initial temperature, properly corrected for subsequent change in barometric pressure.

The time of exposure varied from 66 to 120 hours. The slit-width varied from 0.01 to 0.04 mm, being usually 0.02 mm. The theoretical resolving power of the grating (a 6-inch, 14,438-line grating), for the slit-width used, was actually obtained on all exposures except those in the red where, in the second order, the grating has a somewhat poorer definition.

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[1] See Baly, *Spectroscopy*, p. 241, 1912 edition.

[2] *Zeitschr. f. Wiss. Phot.*, 12, 101, 1913.

The spectrum was photographed on eight different plates, two for each region. These regions were (1) λ 6900–λ 6300, (2) λ 6400–λ 5800, (3) λ 5900–λ 5500, (4) λ 5600–λ 5000. For regions (1) and (2), one was a Cramer plate, the duplicate a Wratten & Wainwright plate. No plates were exact duplicates, as the slit-width and time of exposure were varied. One 85-minute exposure was made on a Hilger spectroscope, for the region λ 6800–λ 7700. A one-minute exposure is sufficient, on this instrument, for the shorter wave-lengths. The spectroscope was calibrated with the argon spectrum, and the readings obtained for nitrogen are probably correct to 1 Å. All of the plates obtained with the large grating are usable save one in the λ 6300–λ 6900 region which dried very unevenly. The duplicate plate, however, is the best that I have, and the readings obtained from it are believed to be as trustworthy as those in any portion of the spectrum.

The work that has thus far been completed is as follows:

1. The lines in the immediate vicinity of the three conspicuous "heads" of each band have been measured, and their wave-lengths computed, on all plates.

2. The regions λ 5500–λ 5900 and λ 6300–λ 6900 have been completely measured and computed.

There are about 6400 lines between λ 5000 and λ 6800, and 274 in the λ 6623 band, in which von der Helm measured 119. There appear to be fully as many in all the other bands, although in most cases the number actually measured is much less, owing to the smaller intensity and shorter length of the bands.

The measurements were made on a 55-cm Geneva dividing engine. The screw was carefully calibrated by the author and is believed to have no unknown errors greater than 0.002 mm. In order to test the evenness of drying of the plates, the international secondary standards were first corrected for non-normality of the dispersion and errors of the screw, and were then fitted as nearly as possible to a linear scale. Only standards of suitable intensity were used, those overexposed being evidently untrustworthy. In the case of one plate in the λ 6300–λ 6900 region, the average deviation of all the normals from a linear scale was less than 0.002 A. This was taken to indicate that the screw had been correctly calibrated. On other plates there was a general drift from such a linear scale, very evidently due to uneven drying. It seldom exceeded 0.015 A and by drawing a smooth curve through the plotted readings of the normals, the correction for this was easily made.

When the wave-length determinations of one plate were compared with those of a duplicate plate, there generally appeared a constant difference between them. This difference varied from 0.01 A to 0.04 A on different sets of plates. It was considered due to the uneven illumination of the grating, as already explained. Fortunately, however, we have interferometer measurements of the three mercury lines present on my plates. By means of the ghosts and satellites of these lines, it was possible to determine their position with great accuracy, in spite of their overexposure. This settled the absolute wave-lengths from λ 5100 to λ 5900. One plate in each of the other two regions was then found to agree perfectly in the overlapping portions. I thus had a full set of plates in complete agreement, and the duplicate plates were then given the proper constant correction to make them also agree.

The values of the wave-length of any one line, as determined on different plates, then seldom differed by more than 0.01 A. Several settings were made on each line, and as the nitrogen lines are fairly sharp, the average experimental error of setting scarcely exceeds 0.003 A. It is hoped, therefore, that the relative error of all save very faint or hazy lines is less than 0.005 A, and that the absolute wave-lengths are in general correct to 0.01 A.

Table I gives the wave-lengths of 872 lines forming the three principal heads of the bands. The lines in the vicinity of all the heads given by von der Helm were measured, although in several cases there is no real head present. Several other heads not given by von der Helm were noted and measured. These so-called "heads" are caused by the proximity of several heavy lines, accompanied by more or less continuous radiation. The measurements, in all cases, cover this region of continuous radiation, which is indicated in the table by braces. Frequently the haze is due merely to the scattering of light in the photographic film, but in most cases it is apparently a true radiation.

The three main heads of a band, out of the five that appear with low dispersion, are designated I, II, and IV. The bands themselves are designated in two ways: first, by the division into groups (*a* to *f*), the individual bands of each group, from red to violet, being designated by Arabic numerals; the second method of designation is that proposed by Cuthbertson[1] and formulated mathematically by Deslandres.[2] In this arrangement the position of the first head of each of the entire set of 57 bands is given as a function of two independent parameters, p and n. The value of these parameters, for each band, is given immediately below the designation of the band according to the first arrangement. The first integer refers to the value of p, the second to n—the values being those of Deslandres.[3]

The three columns in the table are:

(1) Intensity; lines marked " ?" are so faint as to preclude an accurate determination of wave-length; (2) wave-length—on the International System (I.A.), at 15° C., 760 mm; (3) character of the line. In this regard the following abbreviations are used:

s.,	especially sharp.
b.,	broad.
b.d.,	broad, probably double.
d.,	certainly double.
h.,	hazy.
h.r.,	haze on the red side (due to one or more fainter components on that side).
h.v.,	haze on violet side.
n.s.,	a non-symmetric line due to two or more components of unequal intensity. The setting was made on the center of gravity of the system.
k.,	the line at which a "head" apparently starts.
a.,	argon.

Von der Helm's value for the wave-length *in air* for the general position of the head, together with the frequency *in vacuo*, is given to the right of the designation of the head.

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[1] *Phil. Mag.* (6), 3, 348, 1902.

[2] *Comptes rendus*, 134, 747, 1902.

[3] See Baly, *Spectroscopy*, p. 620, 1912 edition.

TABLE I

1	2	3
I *d* 4 48–53	6787.91 17,728.1	
1	6788.614	k.
1	.243	
1	.101	
1	87.970	
2	.834	
2	.712	
1	.515	
2	.270	
II *d* 4 48–53	6778.35 14,748.9	
1	6779.972	
1	78.821	
1	.623	k.
2	.448	
2	77.949	
1	.538	
1	.288	
2	76.874	
2	.661	
IV *d* 4 48–53	6758.98 14,791.2	
2	6759.243	
2	58.054	k.
1	57.807	
1	.665	
2	.355	
1	.067	
1	56.721	
1	.611	
1	.325	
4	55.948	
I *d* 5 47–52	6704.45 14,911.4	
3	6704.755	k.
2	.634	
1	.514	
3	.363	
3	.132	
3	03.879	h.d.
3	.630	
3	.376	
4	.227	
II *d* 5 47–52	6694.95 14,932.6	
4	6694.911	k.
2	.775	
1	.553	
2	.391	
3	.226	n.s. h.v.
2	93.774	
1	.610	b.
1	.474	
3	.367	
3	.242	
3	92.849	
IV *d* 5 47–52	6675.01 14,977.2	
3	6674.908	k.b.
2	.634	b.
4	.230	
2	.074	
2	73.817	
3	.615	
1	.446	
4	72.954	
4	.852	
I *d* 6 46–51	6623.534 15,093.6	
4	6623.574	k.b.
2	.417	
2	.281	
4	.120	b.h.
4	22.915	
2	.795	
5	.658	
3	.395	b.h.
4	.130	n.s.
4	21.971	s.
3	.838	
II *d* 6 46–51	6614.023 15,115.0	
6	6614.031	k.
2	13.789	h.
4	.678	
3	.514	
3	6613.188	h.r.
4	.061	
2	12.878	h.
2	.759	h.
4	.524	
4	.244	s.
1	.001	
3	11.722	
2	.603	
IV *d* 6 46–51	6594.425 15,160.1	
5	6594.418	k.b.
4	.175	
6	93.739	
2	.598	h.v.
5	.155	
4	92.568	
6	.423	
3	91.936	
2	.781	
I *d* 7 45–50	6544.81 15,275.2	
3	6544.881	k.
3	.716	
1	.598	
5	.432	h.
4	.237	
2	.095	
6	43.942	
2	.714	
2	.616	
4	.460	
4	.251	
II *d* 7 45–50	6535.50 15,296.8	
5	6535.655	s.
6	.110	d.
3	34.924	
4	.627	
3	.482	
4	.188	h.r.
3	.028	
4	33.754	h.r. h.v.
1	.305	
4	.127	b.

TABLE I—*Continued*

1	2	3
IV *d* 7 45–50	6516.44 15,341.6	
2	6516.610	
4	.403	h.r.k.
2	.256	h.
2	.166	h.
5	15.897	
6	.759	
1	.586	
2	.407	
4	.181	
6	14.687	
5	.459	
I *d* 8 44–49	6468.53 15,455.3	
4	6468.597	k.b.
4	.438	
5	.144	h.r. h.v.
4	67.951	
2	.802	
6	.634	
2	.416	
3	.280	
3	.142	
4	66.913	
2	.809	
2	.588	
5	.442	b.
II *d* 8 44–49	6459.04 15,478.1	
6	6459.673	
2	.181	
5	58.884	k.
2	.726	h.
3	.503	
2	.385	
4	.261	
2	.128	
2	57.810	
4	.669	
2	.469	h.d.
3	.086	
IV *d* 8 44–49	6440.80 15,521.8	
2	6441.134	
4	40.768	k.h.d.
3	.563	
2	.392	
4	.150	
2	39.992	
3	.590	
4	.270	
4	.168	
5	38.887	
I *d* 9 43–48	6394.45 15,634.2	
2	6394.628	k.
3	.442	
1	.284	
2	.122	
3	93.991	h.v.
1	.854	
5	.636	
II *d* 9 43–48	6384.93 15,657.6	
2	6386.096	
4	85.978	
2	.503	
3	.026	k.
3	84.900	
4	.627	d.
3	.451	b.
2	.322	
2	.081	
4	83.887	b.
IV *d* 9 43–48	6367.55 15,700.3	
4	6367.416	h.r.
2	.165	
4	66.808	
2	.252	
3	.107	
3	65.913	
3	.564	
I *d* 10 42–47	6322.73 15,811.6	
2	6322.816	k.h.
?	.708	
2	.594	
1	.462	
1	.386	
2	.280	
1	.162	
2	.003	n.s.
4	21.797	n.s.
II *d* 10 42–47	6313.20 15,835.5	
4	6314.420	
2	13.287	k.
2	.185	h.
2	.069	
1	12.957	
2	.720	h.
2	.626	h.
1	.214	h.
4	11.659	
IV *d* 10 42–47	6296.03 15,878.8	
3	6296.212	b.h.
1	.026	n.s.
?	95.805	
3	.606	
3	.077	
I *d* 11 41–46	6252.81 15,988.4	
1	6253.001	b.k.
2	52.806	
?	.670	h.
?	.587	h.
1	.494	
1	.377	
1	.226	b.
II *d* 11 41–46	6243.51 16,012.2	
?	6243.688	
2	.581	s.h.v.
2	.297	
1	42.944	h.r.
1	.744	

TABLE I—*Continued*

1	2	3
1	6242.601	
?	.402	h.
3	.199	
IV *d* 11 41–46	6227.00 16,054.7	
2	6227.096	h.k.
3	26.978	b.h.
1	.790	h.
2	.416	
1	.079	h.
I *e* 1 49–53	6185.44 16,162.6	
?	6187.022	h.r.
1	86.733	k.
2	.297	b.h.
1	85.874	
1	.570	b.
I *d* 12 40–45		
1	6185.224	
1	.127	
?	84.937	d.
1	.750	b.
1	.516	b.
1	.313	b.
1	.120	s.
1	.012	s.
?	83.861	
II *e* 1 ? 49–53		
2	6178.549	
2	.170	
?	77.574	
?	.385	
2	.259	
?	76.809	
II *d* 12 40–45	6175.32 16,189.1	
2	6176.126	k.
1	75.967	
?	.791	
?	.654	
1	.523	
1	.392	
1	.251	
1	.112	
2	74.874	
3	.612	
IV *e* 1 ? 49–53		
2	6161.648	
1	.276	
1	.131	
?	60.797	
?	.580	
1	.395	b.
IV *d* 12 40–45	6160.43 16,228.2	
1	6159.844	h.k.
2	.692	h.
?	.443	
2	.114	
1	58.952	h.
1	.581	h.
2	.433	
2	57.960	d.
I *e* 2 48–52	6127.23 16,316.1	
2	6127.374	h.v.k.
1	.208	
1	.087	
4	26.944	
1	.752	
2	.471	
II *e* 2 48–52	6119.79 16,336.0	
2	6120.602	
2	.273	h.v.
1	19.849	k.
2	.720	h.v.
3	6119.454	
1	.312	b.
2	.129	b.
1	18.993	
IV *e* 2 48–52	6102.60 16,382.0	
2	6102.736	k.
1	.514	
3	.381	
1	.259	
2	01.537	
I *e* 3 47–51	6069.60 16,471.0	
5	6069.663	b.k.
2	.463	
5	.280	h.v.
3	.174	
2	.034	h.v.
5	68.704	
1	.506	
3	.382	
2	.250	
II *e* 3 47–51	6062.44 16,490.5	
3	6062.563	
2	.414	
2	.190	h.r.
6	61.984	b.
3	.500	h.r.
IV *e* 3 47–51	6045.55 16,536.6	
3	6045.484	k.
3	.407	
6	.173	h.r.
1	44.970	d.
2	.808	
4	.319	h.r. h.v.
I *e* 4 46–50	6013.60 16,624.4	

TABLE I—*Continued*

1	2	3
5	6013.575	k.h.r.
3	.335	
6	.195	s.
4	.030	
2	12.907	
3	.772	b.
4	.567	
II *e* 4 46–50	6006.34 16,644.5	
4	6006.477	
2	.341	
5	.118	
4	05.967	
3	.834	
4	.645	b.
IV *e* 4 46–50	5990.01 16,689.9	
4	5989.812	n.s.k.
5	.636	s.
3	.519	
1	.324	
2	.179	
4	88.702	
I *e* 5 45–49	5959.25 16,776.0	
2	5959.220	
5	.053	h.v.k.
3	58.767	
5	.656	b.
2	.548	
3	.447	
2	.342	
3	.206	
II *e* 5 45–49	5952.02 16,796.4	
4	5951.935	h.k.
5	.782	
4	.617	
3	.440	
1	.332	
2	.115	
2	.010	
IV *e* 5 45–49	5935.95 16,841.9	
3	5935.920	
3	.740	k.
4	.660	h.r.
3	.553	
5	.426	
1	.231	
3	.092	
1	34.925	
3	.774	
5	.627	
I *e* 6 44–48	5906.24 16,926.6	
5	5906.010	b.k.
1	05.900	
?	.792	
6	.672	h.v.b.
2	.503	
3	.368	
2	.285	
2	.126	
3	04.948	s.
3	.852	
II *e* 6 44–48	5899.19 16,946.7	
2	5899.070	
5	98.930	n.s.k.
2	.631	
2	.523	
3	.401	b.
?	.252	
1	.148	
3	.040	b.
3	97.874	
IV *e* 6 44–48	5883.49 16,992.0	
2	5883.517	
2	.446	
5	.146	k.
5	.029	
1	82.917	
3	.807	
2	5882.615	h.
3	.479	h.
3	.320	
6	.016	h.v. h.r.
I *e* 7 43–47	5854.69 17,075.6	
5	5854.404	b.d.k.
2	.253	
2	.168	
7	.032	b.
3	53.873	
4	.666	h.r.
2	.462	
4	.286	
2	.168	s.
II *e* 7 43–47	5847.67 17,096.1	
?	5847.740	
5	.518	s.k.
1	.405	
2	.300	
2	.243	
1	.120	
2	.040	
6	46.815	b.h.
1	.578	h.r.
5	.477	h.r.
4	.111	h.
IV *e* 7 43–47	5832.29 17,141.2	
3	5832.054	k.
6	31.881	
1	.707	
3	.597	
1	.405	b.
3	.274	
?	.119	
2	30.941	
4	.839	
I *e* 8 42–46	5804.28 17,224.0	

TABLE I—*Continued*

1	2	3
6	5804.135	b.k.
1	03.978	
8	.776	d.
3	.590	
1	.482	
4	.367	
2	.195	
2	.123	
3	02.980	
3	.858	
II *e* 8 42–46	5797.23 17,244.9	
5	5797.451	h.r.
?	.308	
6	.062	
1	96.969	
3	.830	
?	.707	
5	.602	
2	.513	
2	.412	b.
2	.299	
IV *e* 8 42–46	5782.23 17,289.1	
5	5782.307	
8	.059	b.k.
1	81.943	
1	.849	
5	.740	
3	.566	
3	.426	
4	.239	
6	80.984	
4	.836	
I *e* 9 41–45	5755.20 17,370.8	
2	5755.415	
4	.188	h.k.
?	.074	
3	54.983	
5	.862	
5	.746	
4	.616	
1	.498	
6	.366	
2	.195	h.v.
II *e* 9 41–45	5748.18 17,392.0	
5	5748.664	
1	.289	
5	.101	k.
1	.008	
3	47.883	b.
8	.650	b.
6	.408	s.
2	.178	
2	.040	
1	46.939	h.v.
8	.615	
1	.487	
1	.250	h.
2	.149	
IV *e* 9 41–45	5733.68 17,436.0	
4	5733.830	
4	.555	k.
4	.450	
1	.369	
2	.276	
4	.159	s.
1	32.992	
3	.830	b.
1	.703	
9	.462	
1	.279	
2	31.921	
I *e* 10 40–44	5707.49 17,516.0	
3	5707.580	k?
2	.462	h.
1	.301	
2	.131	b.
?	06.944	
?	.840	
3	.597	h.
II *e* 10 40–44	5699.50 17,540.6	
3	5701.358	
2	00.939	
?	.883	
2	5700.637	
2	.512	
?	5699.830	
IV *e* 10 40–44	5685.56 17,583.7	
?	5685.496	
1	.199	
1	.058	b.
I *e* 11 39–43	5660.54 17,661.4	
1	5660.842	k.
?	.590	
?	.421	
1	.331	
1	.240	
1	.115	
2	59.954	b.
II *e* 11 39–43	5653.31 17,683.9	
?	5653.504	s.h.r.
?	.170	
?	52.676	
?	51.841	s.
IV *e* 11 39–43	5639.17 17,728.2	
?	5639.349	
?	38.868	
?	37.899	
?	.775	
I *f* 1 49–52		
Haze 5632.754 to 5632.361 Very faint lines to 5627.750		
II *f* 1 49–52	5622.97 17,779.3	
?	5622.610	

TABLE I—*Continued*

1	2	3
I *e* 12 38–42	5615.00 17,804.5	
1	5615.318	k.
?	.230	
2	.032	b.
1	14.900	b.
1	.779	
1	.695	
1	.573	
1	.387	d.
?	.230	
II *e* 12 38–42	5607.73 17,827.6	
1	5608.214	k.
?	.094	
?	07.687	
?	.375	
I *f* 2 48–51	5592.57 17,876.0	
?	5593.014	
3	92.881	h.v.k.
1	.657	
4	.514	
2	.364	h.
2	.283	h.
2	.130	
1	.013	
?	91.888	
?	.768	
1	.586	
II *f* 2 48–51		
2	5588.081	k.
?	87.989	
1	.883	
2	.742	b.n.s.
3	.531	h.
3	.440	h.
1	.190	
2	.064	
?	86.020	
2	.490	
2	.330	
IV *f* 2 48–51	.	
2	5573.126	s.
2	72.894	
1	.737	
2	.551	a.
2	.347	h.r.k.
3	.247	
2	.039	
1	71.881	
3	.780	
1	.638	
2	.410	s.
2	.320	s.
I *e* 13 37–41	5570.60 17,946.5	
3	5570.777	k.h.
1	.679	
4	.501	b.h.
2	.354	
2	.201	d.
2	.013	h.v.
2	69.850	
2	.786	
II *e* 13 37–41	5563.48 17,969.4	
2	5563.704	
1	.571	
3	.244	b.k.
?	.124	
1	.038	
?	62.937	
?	.828	
?	.696	
?	.612	
1	.405	b.h.
I *f* 3 47–50	5553.63 18,001.2	
2	5554.258	
2	.130	
2	5553.996	
2	.924	
5	.730	b.h.k.
2	.600	
2	.491	
6	.362	b.h.v.
4	.204	b.h.
3	52.962	
II *f* 3 47–50	5548.40 18,018.2	
2	5548.825	
3	.711	
1	.600	
1	.515	
3	.390	
2	.242	
1	.137	h.
IV *f* 3 47–50	5533.46 18,066.9	
5	5533.504	
3	.406	
1	.238	
1	.164	
1	.041	
4	32.955	h.r.
?	.824	
?	.707	
4	.599	h.r.
1	.473	h.
2	.349	s.
2	.251	s.
2	.146	s.
I *e* 14 36–40	5526.84 18,088.6	
2	5527.150	k.h.
4	.027	
5	26.835	s.
4	.707	
2	.610	
4	.508	
4	.356	
3	.188	
II *e* 14 36–40	5520.11 18,110.6	

TABLE I—*Continued*

1	2	3
3	5519.682	
5	.592	
?	.475	
1	.398	
2	.268	
I *f* 4 46–49	5515.54 18,125.6	
1	5515.758	
8	.594	k.b.
7	.451	b.
5	.239	b.h.
5	.178	
3	.081	
2	14.953	b.
3	.777	h.r.
3	.636	b.h.
2	.496	
2	.325	b.d.
3	.190	d.
II *f* 4 46–49	5510.55 18,142.3	
4	5511.096	h.r.
?	10.998	
?	.929	
4	.835	
4	.638	d.h.v.
1	.488	b.
5	.278	b.
?	.177	
?	.109	
?	.044	
1	09.936	
2	.847	
3	.736	s.
2	.545	s.
4	.434	
3	.316	s.
IV *f* 4 46–49	5495.42 18,192.0	
1	5495.997	
4	.885	a.(?)
2	.763	
3	.692	s.
3	.593	s.
2	.430	h.
1	.343	h.
4	.159	h.r.
I *e* 15 35–39		
5	5484.730	
2	.593	
3	.488	
5	.338	b.k.
3	.225	
3	.094	
3	.018	
3	83.896	
4	.686	h.
3	.476	s.
I *f* 5 45–48	5478.73 18,247.4	
1	5478.575	
7	.471	n.s.k.
3	.266	
6	.124	b.
4	.007	
2	77.912	
2	.804	
2	.656	
2	.601	
II *f* 5 45–48	5473.16 18,266.0	
2	5473.524	k.
2	.468	
4	.313	
3	.190	h.
4	.056	h.
5	72.936	
4	.590	h.v.
5	.485	
2	.316	
1	.228	
2	.131	
IV *f* 5 45–48	5458.22 18,315.9	
4	5458.879	h.k.
3	.759	n.s.
2	.630	h.
2	.554	h.
2	.451	
3	.353	s.
3	.273	s.
3	.139	
2	.008	
3	57.903	
2	.797	
1	.697	
4	.587	
I *f* 6 44–47	5442.25 18,369.7	
2	5442.498	
2	.416	
6	.325	k.
4	.276	
4	.200	
4	.104	
7	41.981	
5	.932	
4	.833	
3	.751	
4	.640	s.
II *f* 6 44–47	5437.03 18,387.3	
5	5437.328	k.d.
2	.197	s.
2	.027	
2	36.957	b.
2	.894	b.
3	.801	
3	.621	
5	.518	
3	.399	s.
IV *f* 6 44–47	5424.17 81,430.9	
1	5423.423	
2	.319	
2	.209	

TABLE I—*Continued*

1	2	3
4	5423.014	
4	22.922	
3	.771	
2	.688	
6	.535	b.
4	.369	
6	.187	b.
1	.035	
I *f* 7 43–46	5407.08 18,489.2	
2	5407.575	
3	.411	b.h.
6	.129	h.r.k.
1	.049	
3	06.979	
3	.876	
6	.785	
4	.730	
3	.590	h.v.
2	.528	
II *f* 7 43–46	5401.83 18,507.1	
4	5401.943	b.
3	.810	k.
4	.689	b.
4	.565	
5	.450	
3	.340	
2	.189	
3	.115	
1	.024	
2	00.924	
6	.654	
IV *f* 7 43–46	5387.82 18,555.3	
2	5388.490	
2	.353	
?	.236	
?	.172	
5	.087	k.
5	.002	
4	87.856	
4	.767	
5	.604	
3	.518	
4	.447	h.
3	.385	h.
3	.283	
1	5387.192	h.
2	.050	
I *f* 8 42–45	5372.78 18,607.2	
2	5373.189	
2	72.976	
7	.820	h.k.
3	.727	
7	.496	b.
3	.390	
3	.223	b.h.
II *f* 8 42–45	5367.41 18,625.8	
4	5367.782	b.
3	.654	b.
3	.527	k.
3	.420	
5	.325	
3	.236	
2	.132	
3	.081	
1	66.973	d.
1	.853	
2	.760	
IV *f* 8 42–45	5353.73 18,673.4	
3	5354.073	k.
3	53.992	
3	.872	b.
1	.768	
6	.608	n.s.
2	.493	
I *f* 9 41–44	5339.27 18,724.0	
2	5339.432	h. k.
1	.393	
3	.294	
1	.192	
1	.089	
?	38.920	d.
II *f* 9 41–44		
2	5334.318	d.
?	.165	
?	.026	b.h.
?	33.878	
3	.762	
IV *f* 9 41–44	5323.40 18,779.8	
1	5323.821	
?	.523	
?	.411	
?	22.983	b.h.
?	.770	b.h.
1	.615	n.s.
?	.483	b.h.
I *f* 10 40–43	5306.22 18,840.0	
1	5307.072	
1	.004	
2	06.859	k.
2	.529	
1	.146	
2	05.980	
1	.696	
2	.413	
II *f* 10 40–43		
2	5302.604	
1	.170	
?	.610	
?	.524	
1	.885	d.
I *f* 11 39–42	5274.35 18,953.9	
1	5275.072	k.
?	74.891	
2	.777	h.h.v.
?	.347	
I *f* 12 38–41	5244.05 19,063.9	
1	5244.071	k.
2	43.782	

TABLE I—*Continued*

1	2	3
I *f* 13 37–40	5213.04 19,177.4	
2	5213.808	k.
3	.540	h.v.
1	.021	
II *f* 13 37–40	5207.79 19,196.7	
2	5209.009	s.
2	08.669	b.h.
1	.503	
3	.300	h.
2	.157	
1	07.885	
3	.558	h.r.
1	.262	h.
2	06.894	s.
2	.800	
4	.024	s.
IV *f* 13 37–40		
3	5196.370	h.v.
?	.196	
1	5196.080	
2	95.967	
1	.679	
2	.443	
2	.346	
2	94.854	
I *f* 14 36–39	5183.84 19,285.4	
3	5184.237	b.k.
4	83.970	b.
1	.843	
1	.734	
1	.679	
1	.550	
2	.445	
2	.394	
II *f* 14 36–39		
4	5179.876	n.s.
3	.567	
1	.460	
2	.322	
3	.217	
2	.072	
1	5178.940	
IV *f* 14 36–39		
2	5167.060	k.
2	66.992	
1	.872	
1	.766	
2	.676	s.
1	.410	
1	.309	
2	.181	
2	.058	
I *f* 15 35–38		
2	5155.323	k.
2	.201	
1	.095	
I *f* 16 34–37		
1	5126.806	k.
?	.726	

The following table (Table II) gives the measurements of all conspicuous lines, or groups of lines, in the bands extending from λ 6800 to λ 7650, as taken on the Hilger spectroscope. The probable error is 1 A.

The three main heads are designated as before, using only the first method of grouping. The columns are: (1) wave-length *in air;* (2) frequency *in vacuo;* (3) designation of head.

Table III gives Croze's measurements of the first head of the bands from λ 7600 to λ 9100. The probable error is several angstroms.

DISCUSSION

The discussion naturally falls into three sections: (1) a brief sketch of the two methods previously proposed for grouping the heads of the nitrogen bands; (2) a quantitative test of the comparative validity of the two methods, based upon the data given

TABLE II

1	2	3	1	2	3	1	2	3
7624.8	13,111.5	I *c* 3	7261.3	13,768.1	II *c* 6	7072.8	14,134.8	
7613.5	13,131.2	II *c* 3	7254.3	13,781.3		7059.6	14,161.2	I *c* 8 I *d* 1
7589.4	13,172.9	IV *c* 3	7250.0	13,789.4				
7505.6	13,319.9	I *c* 4	7239.9	13,808.5	IV *c* 6	7048.5	14,183.7	II *c* 8
7492.2	13,343.7	II *c* 4	7233.1	13,821.6		7040.4	14,200.2	
7469.6	13,383.9	IV *c* 4	7228.5	13,830.9		7028.2	14,224.7	IV *c* 8
7445.3	13,427.6		7221.6	13,843.7		7016.5	14,248.3	
7404.8	13,501.0		7214.0	13,858.3		7001.4	14,279.1	
7386.1	13,535.3	I *c* 5	7205.2	13,875.3		6991.5	14,299.3	
7375.6	13,554.5	II *c* 5	7197.3	13,890.5		6978.6	14,325.9	
7366.8	13,570.7		7181.0	13,921.8		6968.0	14,347.6	I *d* 2
7363.0	13,577.7		7165.0	13,953.0	I *c* 7	6956.0	14,372.3	II *d* 2
7352.8	13,596.5	IV *c* 5	7153.0	13,976.2	II *c* 7	6946.0	14,392.8	
7345.6	13,609.9		7145.2	13,992.0		6938.8	14,408.1	IV *d* 2
7338.3	13,623.3		7142.2	13,997.5		6929.5	14,427.2	
7331.0	13,637.0		7132.2	14,017.2	IV *c* 7	6921.6	14,443.8	
7323.4	13,651.3		7125.0	14,031.4		6906.0	14,476.1	
7315.3	13,666.3		7120.0	14,041.2		6896.6	14,497.2	
7307.7	13,680.6		7112.3	14,056.5		6875.5	14,540.5	I *d* 3
7291.2	13,711.5		7099.3	14,082.0		6865.2	14,562.3	II *d* 3
7274.0	13,743.8	I *c* 6	7090.9	14,098.7				

TABLE III

1	2	3	1	2	3
9101	10,985	I *b* 1	8043	12,430	I *b* 7
8903	11,229	I *b* 2	7887	12,676	I *b* 8 I *c* 1
8707	11,482	I *b* 3			
8541	11,705	I *b* 4	7742	12,913	II *c* 2 (?)
8369	11,946	I *b* 5	7628	13,106	I *c* 3
8204	12,186	I *b* 6			

in the preceding tables; (3) a summary of the evidence in favor of each method, based upon (*a*) the appearance of the bands under high dispersion, and ordinary conditions of excitation (work of the author); and (*b*) the appearance of the bands under low dispersion, but unusual conditions of excitation (work of previous investigators).

SECTION I

The nitrogen lines of wave-length longer than λ 5100, comprising the First Deslandres' Group, fall into 57 similar groups of lines, called "bands." Each band contains several sets (usually five) of particularly heavy and close lines. These sets have been called the "heads" of the bands. That set in each band lying farthest to the red usually ends abruptly on the red side, and has been called head I, the band being said to begin at this point, and to be degraded toward the violet.

In an ordinary band, such as is found in the Second Deslandres' Group of the nitrogen spectrum (λ 5060 to λ 2814) there are series of lines starting at the head, and proceeding with diminishing intensity toward the violet. Near the head, the lines of such a series are so related that successive frequency intervals form an arithmetical series. This is Deslandres' Law for band series. In the First Delandres' Group, however, there appear to be no relationships between the 250 or more lines forming each "band." This is *not*, therefore, an ordinary band spectrum.

Relationships first appear when we group together corresponding lines in successive bands, choosing one line from each band. We might take one line from the first (I) head of the λ 6623 band, another from the first head of the λ 6545 band, etc., and thus form a series. Under low dispersion the set of lines forming a head appears as a single broad line. Thus successive first heads were found to form a series satisfying Deslandres' Law—similarly successive second (II) heads, etc. Such a series extends over 10 to 15 bands, and then the interval between successive terms changes abruptly. Accordingly the ten or more bands represented in such a series have been classified as a "group of bands." The entire First Deslandres' Group is composed of five, and possibly six, such subgroups. which we have designated *a* to *f* respectively. Von der Helm decided that this was the best method for grouping the band heads, and arranged his data in this way. I shall therefore refer to it as the von der Helm arrangement, although it is not original with him.

The second arrangement of the bands was first suggested by Cuthbertson. In this the head of a band in one of the above groups is related, not to the adjacent *band*, but to a band in the adjacent band *group*. In the series thus formed we have only as many terms as we have band groups, and the spacing between terms is much greater than in the von der Helm arrangement. Since a series contains the head of only one band of a group, there are at least as many series as there are bands in a group. It is possible to form

11 such series having at least three terms each, and 6 more having only two terms each.

The reason for such a grouping is that the 17 series thus formed are identical in spacing with one another, and also with the five series into which the bands of the Second Deslandres' Group have been divided. Each series appeared to fulfil Deslandres' Law, and is known as Deslandres' First Progression. Each series, moreover, is displaced relative to the preceding one by a regularly increasing amount. Thus the corresponding terms of the several series form of themselves another set of series, also approximately obeying Deslandres' Law, and known as Deslandres' Second Progression.

Thus the entire set of the first heads of the bands in the First Deslandres' Group can be represented as a function of two parameters, p and n. The variation of n gives the First Progression, that of p the Second. Deslandres considered that both progressions obeyed his law, and wrote the complete formula

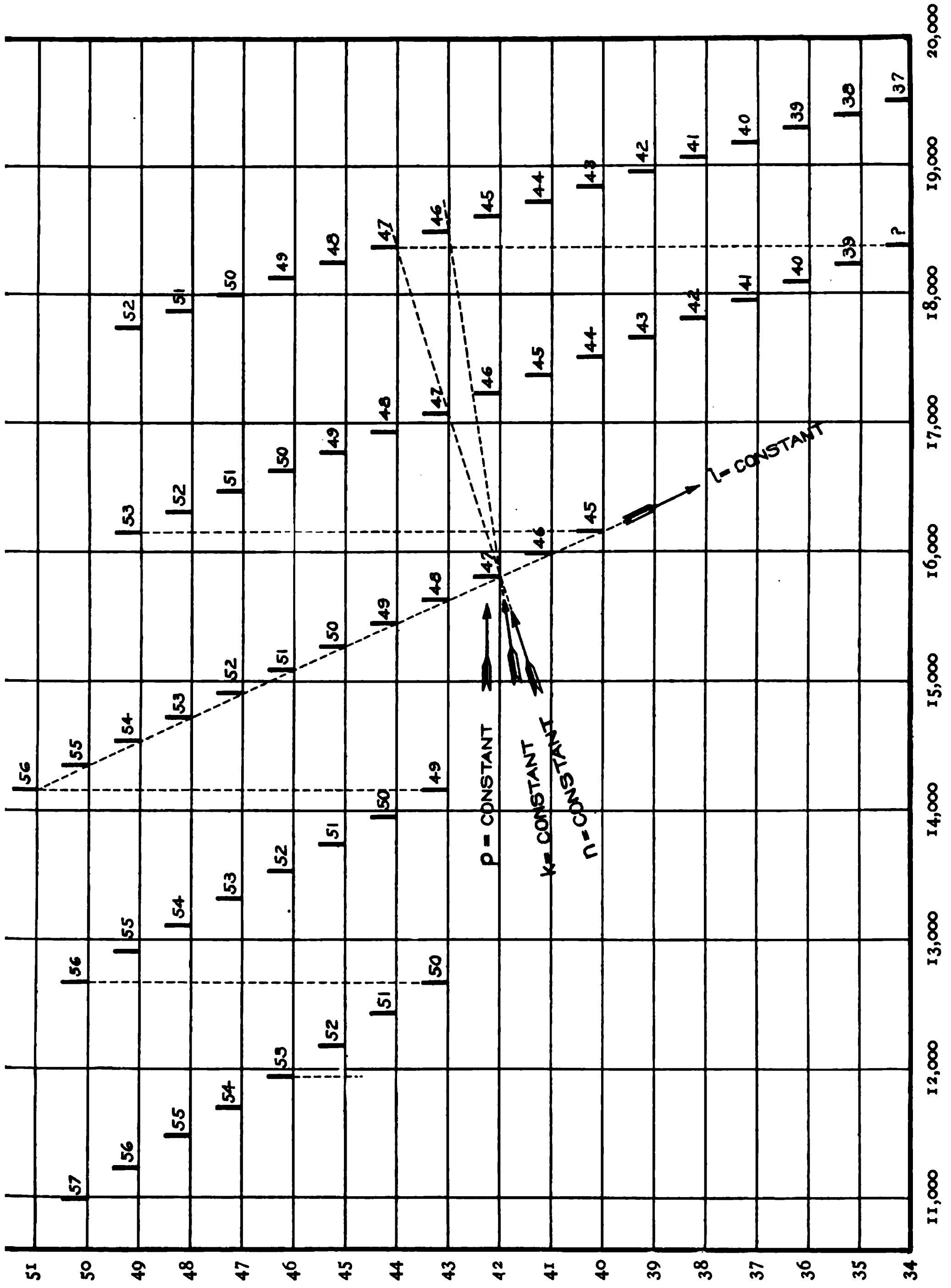
$$v=A+B(n+c_1)^2+C(p+c_2)^2. \qquad (1)$$

In this formula we can make a linear transformation of variables

$$k=\tfrac{1}{2}(p+n) \qquad l=\tfrac{1}{2}(p-n)$$

and obtain $f\ (k, l)$, also of second degree in each parameter, and so giving the ordinary Deslandres' Law when one parameter alone is varied. In such a $f\ (k, l)$ successive integral values of k (l remaining constant) give the heads of the successive bands of one group of the von der Helm arrangement. On the other hand, l has different values for successive band groups.

Fig. 1 may make this clearer. This figure gives the general position of the first head of every band, plotted with frequency as one co-ordinate and the value of p as the other. Any horizontal succession of heads, for which $p=$constant, gives Deslandres' First Progression. The value of n for each head is plotted beside it, and any succession of heads for which $n=$constant gives the Second Progression. The series $l=$constant indicates one of the band groups of the von der Helm arrangement.


p = CONSTANT
k= CONSTANT
n=CONSTANT
l= CONSTANT
11,000
12,000
13,000
14,000
15,000
16,000
17,000
18,000
19,000
20,000
51
50
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36
35
34

FIG. 1

SECTION II

That portion of the nitrogen spectrum under investigation appears to be formed of two superimposed spectra. One of these consists of lines of regular arrangement, the other of lines arranged irregularly. A graph of the lines of several bands of the *e* group indicates that perhaps 50 out of the 250 lines of each band belong to the regular spectrum. These sets of 50 lines have a similar appearance in each band. It is thus possible to identify corresponding lines in successive bands and to form them into series extending through one band group, and obeying Deslandres' Law as a first approximation. I shall call each of the 50 series thus formed a "simple" series.

The first heads of successive bands are composed mainly of several such series, and the general position of the first heads of successive bands, under low dispersion, forms roughly such a series. Table IV gives the simple series of longest wave-length in each band group. It is therefore composed of the "first" heavy line in each band, in the case of all the bands photographed under high dispersion. For the others the approximate position of the edge of the first head is used, as given in Tables II and III. Deslandres' Law demands that the first frequency differences, given in the fifth column, shall form an arithmetical progression, the second differences (sixth column) being a constant. The probable experimental error, in terms of frequency, varies from 0.04 at λ 5000 to 0.02 at λ 6800. Such an average error in the measurements, however, may cause an average variation four times as large in the second differences given in the last column.

Each series evidently obeys Deslandres' Law for the major portion of its extent, but deviates from this law near the violet end of the group. This is true for series in all band spectra, Deslandres' Law holding only near the head of a series. The only formula holding for an entire series is that of Thiele.[1] It contains eight undetermined coefficients and so is very difficult to work with. I have preferred to use simply Deslandres' Law, or a slight modification of it, and to note whether there was a regular deviation from this law.

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[1] *Astrophysical Journal*, 6, 65, 1897.

TABLE IV

Designation		λ (Air)	Frequency (*vacuo*)	First Difference	Second Difference
	p n				
f 16	34–37	5126.81	19,499.86		
				107.88	
f 15	35–38	5155.32	19,391.98		0.27
				108.15	
f 14	36–39	5184.24	19,283.83		1.22
				109.37	
f 13	37–40	5213.81	19,174.46		1.27
				110.64	
f 12	38–41	5244.07	19,063.82		1.39
				112.03	
f 11	39–42	5275.07	18,951.79		1.49
				113.52	
f 10	40–43	5306.86	18,838.27		1.32
				114.84	
f 9	41–44	5339.41	18,723.43		1.58
				116.42	
f 8	42–45	5372.82	18,607.01		1.65
				118.07	
f 7	43–46	5407.13	18,488.94		1.50
				119.57	
f 6	44–47	5442.32	18,369.37		1.62
				121.19	
f 5	45–48	5478.47	18,248.18		1.63
				122.82	
f 4	46–49	5515.59	18,125.36		1.64
				124.46	
f 3	47–50	5553.73	18,000.90		1.55
				126.01	
f 2	48–51	5592.88	17,874.89		0.52
				126.53	
f 1	49–52	5632.75	17,748.36		
e 15	35–39	5484.34	18,228.65		
				141.19	
e 14	36–40	5527.15	18,087.46		0.46
				141.65	
e 13	37–41	5570.78	17,945.81		0.69
				142.34	
e 12	38–42	5615.32	17,803.47		0.83
				143.17	
e 11	39–43	5660.84	17,660.30		1.07
				144.24	
e 10	40–44	5707.46	17,516.06		1.02
				145.26	
e 9	41–45	5755.19	17,370.80		1.23
				146.49	
e 8	42–46	5804.13	17,224.31		1.40
				147.89	
e 7	43–47	5854.40	17,076.42		1.32
				149.21	
e 6	44–48	5906.01	16,927.21		1.46
				150.67	

TABLE IV—*Continued*

Designation		λ (Air)	Frequency (*vacuo*)	First Difference	Second Difference
	p n				
e 5	45–49	5959.05	16,776.54		1.43
				152.10	
e 4	46–50	6013.57	16,624.44		1.52
				153.62	
e 3	47–51	6069.66	16,470.82		1.51
				155.13	
e 2	48–52	6127.37	16,315.69		1.41
				156.54	
e 1	49–53	6186.73	16,159.15		
d 12	40–45	6185.22	16,163.09		
				175.18	
d 11	41–46	6253.00	15,987.91		1.35
				176.53	
d 10	42–47	6322.82	15,811.38		1.03
				177.56	
d 9	43–48	6394.63	15,633.82		1.21
				178.77	
d 8	44–49	6468.60	15,455.05		1.36
				180.13	
d 7	45–50	6544.88	15,274.92		1.34
				181.47	
d 6	46–51	6623.57	15,093.45		1.28
				182.75	
d 5	47–52	6704.75	14,910.70		1.43
				184.18	
d 4	48–53	6788.61	14,726.52		1.8
				186.0	
d 3	49–54	6875.5	14,540.5		
				192.9	
d 2	50–55	6968.0	14,347.6		
				186.4	
d 1	51–56	7059.6	14,161.2		
c 8	43–49	7059.6	14,161.2		
				208.2	
c 7	44–50	7165.0	13,953.0		
				209.2	
c 6	45–51	7274.0	13,743.8		
				208.5	
c 5	46–52	7386.1	13,535.3		
				215.4	
c 4	47–53	7505.6	13,319.9		
				208.4	
c 3	48–54	7624.8	13,111.5		
				198.5 (?)	
c 2	49–55	7742. (?)	12,913. (?)		
				237. (?)	
c 1	50–56	7887.	12,676		
b 8	43–50	7887	12,676		
				246	

TABLE IV—*Continued*

Designation		λ (Air)	Frequency (*vacuo*)	First Difference	Second Difference
	p n				
b 7	44–51	8043	12,430		
				244	
b 6	45–52	8204	12,186		
				240	
b 5	46–53	8369	11,946		
				241	
b 4	47–54	8541	11,705		
				223	
b 3	48–55	8707	11,482		
				253	
b 2	49–56	8903	11,229		
				244	
b 1	50–57	9101	10,985		

In groups *d* and *e* it is occasionally doubtful what line forms the beginning of a new band. In the first heads of the *f* group, however, there appears an extremely heavy doublet, the successive pairs of lines having not only the same relative intensity, but also a constant frequency difference. The doublets thus form two simple series, of which that of longer wave-length has been used for the *f* group of Table IV. In *f* 1 only one member of the doublet is present—that of shorter wave-length. Hence it does not fit well with the other lines in Table IV. I give in Table V the simple series formed from the more refrangible member of the doublet.

The first nine terms of this series can be fitted into the ordinary Deslandres' formula

$$v=A+B(m+c)^2 \qquad (2)$$

with an average difference between observed and computed values of 0.005 A. For the *less* refrangible member of the doublet the corresponding average difference is 0.006 A, and the constants for this latter series are:

$A=22,900.627$
$B=-\ 0.8000$
$c=+\ 0.260$
$m=80$ to 72

The beginning of the deviation from Deslandres' Law occurs, in both series, at a point of minimum intensity at *f* 10 (λ 5306).

TABLE V

Designation		λ (Air)	Frequency (vacuo)	First Difference	Second Difference
	p n				
f 1	49–52	5632.754	17,748.361		
				127.701	
f 2	48–51	5592.514	17,876.062		1.669
				126.032	
f 3	47–50	5553.362	18,002.094		1.597
				124.435	
f 4	46–49	5515.239	18,126.529		1.629
				122.806	
f 5	45–48	5478.124	18,249.335		1.607
				121.199	
f 6	44–47	5441.981	18,370.534		1.615
				119.584	
f 7	43–46	5406.785	18,490.118		1.571
				118.013	
f 8	42–45	5372.496	18,608.131		1.584
				116.429	
f 9	41–44	5339.089	18,724.560		1.544
				114.885	
f 10	40–43	5306.529	18,839.445		1.479
				113.406	
f 11	39–42	5274.777	18,952.851		1.379
				112.027	
f 12	38–41	5243.782	19,064.878		1.448
				110.579	
f 13	37–40	5213.540	19,175.457		1.197
				109.382	
f 14	36–39	5183.970	19,284.839		1.364
				108.018	
f 15	35–38	5155.095	19,392.857		

At this same point the frequency difference of the doublet also begins to diminish. For these two reasons it appears that the *f* group consists really of two groups, having a point of coincidence at λ 5306. Table VI gives the frequency difference of the doublets for the entire *f* group.

I have thus far been unable to find any other strong series lying within the heads of the *f* group. In the *d* and *e* groups, however, there are at least 15 series, distributed among the three heads. In most of these the second difference remains approximately constant for six or eight terms; in a few it forms more nearly an arithmetical progression, the third difference being constant. Such a relation can be satisfied by adding one more term to Deslandres' Law, so that it reads:

$$v=A+B(m+c)^2+C(m+c)^3\,. \qquad (3)$$

TABLE VI

	DESIGNATION						
	f_2	f_3	f_4	f_5	f_6	f_7	f_8
Difference $\left(\text{in } \frac{10^8}{A}\right)$.....	1.173	1.193	1.167	1.157	1.161	1.176	1.123

	DESIGNATION						
	f_9	f_{10}	f_{11}	f_{12}	f_{13}	f_{14}	f_{15}
Difference.............	1.127	1.175	1.064	1.059	1.034	1.006	0.876

In the fifteen series the average difference of experimental and calculated values is slightly more than 0.01 A. In some cases it is over 0.02 A and evidently exceeds the experimental error of measurement. The lines forming the doublets in *f* are very difficult to measure correctly, because of their great intensity, and the nearness of adjacent lines. Yet they fit into series better than any other set of lines. Hence the deviations from formulae (3) or (2), in the case of other series are real, and not due to experimental errors.

The spacing arrangement in different series varies slightly, so that series often tend to cross one another, and this gives successive heads an entirely different appearance. This can best be shown by the five series in heads IV *d*. These five series include nearly two-thirds of all the lines present in these heads, and, with two exceptions, every strong line. Series δ and ϵ start from the same line and gradually diverge. Series δ, at the fifth term, breaks into a doublet, the components of which in turn diverge. The middle of the doublet is used for the last two terms. Such a sudden splitting of a line into a doublet is common in the series found in band spectra, and there are numerous examples of it in the spectrum under investigation. The five series are given in Table VII.

The foregoing portion of Section II has been concerned simply with the law followed by individual simple series, each being considered entirely independently. There are also relationships

TABLE VII

IV d α

λ (Air)	Frequency (*vacuo*)	First Difference	Second Difference
6758.054	14,793.111		
		184.265	
6674.908	14,977.376		1.460
		182.805	
6594.418	15,160.181		1.312
		181.493	
6516.403	15,341.674		1.340
		180.153	
6440.768	15,521.827		1.349
		178.804	
6367.416	15,700.631		1.251
		177.553	
6296.212	15,878.184		1.020
		176.533	
6226.978	16,054.717		1.165
		175.368	
6159.692	16,230.085		

IV d β

λ (Air)	Frequency (*vacuo*)	First Difference	Second Difference
6757.355	14,794.642		
		184.242	
6674.236	14,978.884		1.383
		182.859	
6593.739	15,161.743		1.411
		181.448	
6515.759	15,343.191		1.322
		180.126	
6440.150	15,523.317		1.311
		178.815	
6366.808	15,702.132		1.234
		177.581	
6295.606	15,879.713		1.127
		176.454	
6226.416	16,056.167		1.012
		175.442	
6159.114	16,231.609		

IV d γ

λ (Air)	Frequency (*vacuo*)	First Difference	Second Difference
6756.666	14,796.151		
		184.127	
6673.615	14,980.278		1.320
		182.807	
6593.155	15,163.085		1.340
		181.467	
6515.181	15,344.552		1.352
		180.115	
6439.590	15,524.667		1.272
		178.843	
6366.252	15,703.510		1.306
		177.537	
6295.077	15,881.047		

TABLE VII—*Continued*

IV d δ

λ (Air)	Frequency (*vacuo*)	First Difference	Second Difference
6755.948	14,797.724		
		184.040	
6672.954	14,981.764		1.368
		182.672	
6592.568	15,164.436		1.393
		181.279	
6514.687	15,345.715		1.435
		179.844	
6439.220	15,525.559		1.304
		178.540	
6366.010	15,704.099		

IV d ϵ

λ (Air)	Frequency (*vacuo*)	First Difference	Second Difference
6755.948	14,797.724		
		184.268	
6672.852	14,981.992		1.491
		182.777	
6592.423	15,164.769		1.293
		181.484	
6514.459	15,346.253		1.374
		180.110	
6438.887	15,526.363		1.273
		178.837	
6365.564	15,705.200		

between the spacing arrangement of simple series in different band groups. This can best be studied from the standpoint of the Cuthbertson arrangement.

In a two-parameter formula such as (1) there may be included one line from each band in the entire spectrum. It therefore comprises several simple series. The entire set of simple series, one for each band group, satisfying separately and collectively such a two-parameter formula I call a "complete" series. When the lines of any complete series are regrouped to form the p and n progressions, it appears that formula (1) is not the correct functional form. Table VIII shows this clearly. In this table I give only the average frequency intervals of the two progressions, using the data given in Table IV.

TABLE VIII

First Progression p=Constant			Second Progression n=Constant		
n	First Frequency Difference	Second Frequency Difference	p	First Frequency Difference	Second Frequency Difference
54			49		
	1615.0			1432.3	
53		25.6	48		27.3
	1589.4			1405.0	
52		29.9	47		28.0
	1559.5			1377.0	
51		28.9	46		27.8
	1530.6			1349.2	
50		29.0	45		27.8
	1501.6			1321.4	
49		29.6	44		28.0
	1472.0			1293.4	
48		29.6	43		28.6
	1442.4			1264.8	
47		29.7	42		28.5
	1412.7			1236.3	
46		29.9	41		28.9
	1382.8			1207.4	
45		30.2	40		29.4
	1352.6			1178.0	
44		30.3	39		29.7
	1322.3			1148.3	
43		30.8	38		30.3
	1291.5			1118.0	
42		31.2	37		31.0
	1260.3			1087.0	
41		31.6	36		31.0
	1228.7			1056.0	
40		32.4	35		33.4
	1196.3			1022.6	
39		31.3	34		
	1165.0				
38		34.5			
	1130.5				
37					

The second difference is an approximate arithmetical progression and requires a function of the type given in formula (3). Instead of formula (1) we must therefore use:

$$v=A+B(n+c_1)^2+r(n+c_1)^3+C(p+c_2)^2+s(p+c_2)^3\,. \qquad (4)$$

Since the variation of both n and p has the same functional form, it follows that the variation of both together, such as we find in a simple series, has also this same form. For that reason it is possible to combine two simple series in order to determine the constants of a complete series. The two conditions imposed upon such a pair of simple series are: (1) each simple series must fit formula (3); (2) both simple series must have the same third difference.

In formula (3) this third difference equals $6C$; in (4) it is $6(r+s)$. It is therefore the same for both simple series. When the constants of a complete series are thus determined, all other simple series included in the complete series have definite predicted positions.

If we now choose the simple series given in Table IV, using only the band groups for which we have accurate measurements (groups *f*, *e*, and part of *d*), it appears that all three simple series satisfy condition (1), but no two of them satisfy condition (2). It is therefore impossible to group them together into a complete series satisfying formula (4), and so the first lines of the first heads of all bands do *not* satisfy the Cuthbertson arrangement. Another way of stating this is that the several First Progressions are not identical with one another. This was evident in compiling Table VIII. There are eight intervals in this table whose values can each be derived from two different First Progressions (and similarly for the Second Progressions), using only accurate data. For these eight intervals the average difference of the two values is 0.2 A, more than ten times the experimental error.

In the I heads of the *d* group there are three heavy lines in all. The two of shorter wave-length form a doublet of the same constant frequency difference as that in the *f* group. This suggested the combination of these two series of doublets into two complete series, which should differ from one another only by a constant value. It appears that the two simple series formed from the doublets in the *d* group are compatible with those of the *f* group, and so this rearrangement into complete series is possible.

The simple series in the *d* group, of shorter wave-length, is given in Table IX.

Using the two simple series given in Tables V and IX, we get the following constants for the complete series. The derivation is rather laborious, and the computations were not made by a strictly least-squares method:

$A = 22{,}108.476$ $\quad r = +0.0245$
$B = -\ 18.0562$ $\quad s = -\ .0254$
$C = +\ 17.2474$ $\quad c_1 = +\ .3365$
$\quad c_2 = +\ .7222$

For p and n the derived values are respectively three and four units lower than Deslandres' values, which I have consistently used in designating the bands. This shows not only that the values of c_1 and c_2 (which define the "phase" of a series) are meaningless without more accurate data, but also that no deductions can be drawn from the exact value of $p-n$ for any band group.

TABLE IX

Designation		λ (Air)	Frequency (vacuo)	First Difference	Second Difference
	p n				
d 4	48–53	6787.712	14,728.479		
				184.174	
d 5	47–52	6703.879	14,912.653		1.291
				182.883	
d 6	46–51	6622.658	15,095.536		1.306
				181.577	
d 7	45–50	6543.942	15,277.113		1.335
				180.242	
d 8	44–49	6467.634	15,457.355		1.352
				178.890	
d 9	43–48	6393.636	15,636.245		1.210
				177.680	
d 10	42–47	6321.797	15,813.925		

For eight terms from the f group, and seven from the d group, the average difference (obs.—calc.) is 0.005 A. For the less refrangible member of the doublet we have

$$A=22,107.315$$

The other constants remain the same. For 14 terms the average difference (obs.—calc.) is 0.01 A.

By means of the constants given above we can obtain the theoretical position of corresponding simple series in all other band groups. From the position of the component simple series, in the heads of the d and f groups, we should expect the predicted series in the b and c groups to lie just to the violet of the rough measurements of the first heads in those groups. This is found to be the case, within the limits of experimental error. In the e group, however, where we have accurate data, there is no series in the predicted position. All series in I e have a slightly different spacing arrangement, and one of them gradually crosses the predicted series.

Thus the only Cuthbertson arrangement I have been able to get is between alternate rather than adjacent groups. As already pointed out, $k \ \{=\frac{1}{2}(p+n)\}$ and $l \ \{=\frac{1}{2}(p-n)\}$ are the parameters in the von der Helm arrangement, corresponding to p and n in the Cuthbertson arrangement. In this latter arrangement the first heads of all the bands are represented by integral values of p and n. In the von der Helm arrangement integral values of k give a simple series. If, however, we keep k constant, and give l successive integral values, we get corresponding first heads only in every alternate band group. (See series k=constant on Fig. 1.) For the intermediate groups l has the value of an integer plus one-half, and cannot be satisfied by integral values of p and n. Therefore we might expect to find related simple series only in every alternate group. I have at present no other numerical evidence either for or against this view.

The previous discussion shows that many more lines can be fitted into series on the von der Helm arrangement than on the Cuthbertson. This naturally follows from the fact that each simple series involves only one parameter, while the Cuthbertson arrangement involves two. The individual series in different band groups should have related spacing arrangements, given implicitly by formula (4). The data show, however, that the relation is in general not accurate within the limits of experimental error.

One further point of interest is the continuity of successive band groups. The heads of the last band of one group practically coincide with those of the first band of the succeeding group. In this connection the band at λ 6186 is the most interesting in the entire spectrum. In this band we have at 6186.7 a head which agrees in its general position and appearance with the designation I *e* 1; similarly at 6185.2 a head I *d* 12. The entire appearance of the band is that of a *d* band, and it is doubtful whether the *e* group is represented save by I *e* 1, although I have recorded in Table I the lines in the vicinity of the theoretical position of II *e* 1 and IV *e* 1.

In the case of the *e* and *f* groups, the theoretical position of I *e* 16 is 5443.3, almost coinciding with the strong I *f* 6 head at 5442.3. Deslandres records I *e* 16 but there seem to be no lines at this point resembling an *e* head. Again, however, the rough theoretical positions of these two heads almost coincide. For the other groups the coincidences are at 7059.6 and 7887. The data are so inaccurate here that the positions will fit equally well in either of the adjacent band groups. Considering that we have at least approximate coincidences at the four points mentioned above, several interesting relations follow.

The values of p and n at these points are:

$$\begin{array}{llll} \quad p\quad n & \quad p\quad n & \quad p\quad n & \quad p\quad n \\ 1\begin{cases}43\text{–}50\\50\text{–}56\end{cases} & 2\begin{cases}43\text{–}49\\51\text{–}56\end{cases} & 3\begin{cases}40\text{–}45\\49\text{–}53\end{cases} & 4\begin{cases}34\text{–}38\\44\text{–}47\end{cases}\end{array}$$

Since the coincidence is between two heads of different band groups, the two values of $p-n$ at each point differ by unity. Two other unexpected facts, however, are: (1) that the discontinuity in p increases by unity at each succeeding point of coincidence; and (2) that the number of bands between points of coincidence increases by four, from group to group. This is also shown in Fig. 1. The coincident points are indicated by vertical dotted lines. The length of these lines gives the discontinuity in p. The number of bands between them is seen to increase by four, as one goes from red to violet. In group *c* there are six, in *d* ten, and in *e* fourteen bands.

If this rule were followed farther to the red we should expect only two bands in *b*, between the coincident bands 46–53 and 43–50. This would be the last group, the next one, by rule, having zero length. On the violet side we should expect nine more bands (including the coincident ones) in the *f* group, 25–28 coinciding with 36–38 of an unknown *g* group, and so on. In the next (*h*) group the last of the 26 predicted bands would have $p=-1$, $n=0$. Since the correct value of $p-n$ for any band group is indeterminate to at least one integer, it seems natural to suppose that all values of p should be raised by one integer.

We should then have a complete plan for the First Deslandres' Group. It would start, theoretically, at $p=0$, $n=0$, and would consist of seven groups of bands. The first head of some band near the end of each group would coincide approximately with the first head of a band in the next group. The number of bands between coïncidences would diminish by four, in each succeeding group. Some groups run past the points of coincidence and so overlap on each other.

Although groups *g* and *h* do not appear in the ordinary spectrum, Goldstein[1] believes he has seen the First Deslandres' Group, under certain low-temperature conditions, extending into the blue. Other investigators have been unable to verify this. Group *h* should start at λ 4430 and extend to λ 4530. Group *g* should extend from this latter point to λ 4890, and *f* from λ 4890 to λ 5442.8.

SECTION III

Under high dispersion successive bands have a very similar appearance, and this not only suggested to the author the formation of simple series, but also indicates the validity of the von der Helm arrangement of the bands. The general intensity of successive bands also varies continuously through a group of bands. All simple series were formed from lines of the same general appearance, and of a continuously varying intensity. The large number of possible series with approximately the same spacing is also good evidence of a connection between successive lines.

A few bands in group *e* have been measured and plotted beneath one another. It is these bands (λ 5900–λ 5700) that indicate the existence of some 50 simple series of lines, superimposed upon a much larger number of unrelated lines. Below λ 5700 all of the *e* series die out, save only those in the first heads. In the *d* group, however, the series extend to the last regular *d* band at λ 6185, and perhaps farther. In the case of the *f* group there seem to be no conspicuous series save the two mentioned in the first heads. This portion is the most irregular of the entire spectrum.

The only exceptions to the general rise and fall of intensity in the bands of one group are two very strong heads at λ 7072.8 and λ 6968.0. The latter lies at the predicted position of I *d* 2. The former lies somewhat to the red of I *c* 8. There is no apparent reason why either one should be strong.

On the other hand, all changes in appearance of the bands under changing physical conditions point to the Cuthbertson arrangement as the one indicating the actual physical connection between the sources of the radiation. Fowler[1] has shown that the spectrum of the active modification of nitrogen shows certain of the bands of the First Deslandres' Group greatly intensified, while the others are very faint or entirely lacking. The three strongest bands are those at λ 6253, λ 5804, and λ 5407 ($n=46$; $p=41$, 42, and 43), while the weaker bands on each side are those at λ 6323, λ 5854, λ 5442 ($n=47$; $p=42$, 43, 44) and at λ 6185, λ 5755, and λ 5373 ($n=45$, $p=40$, 41, and 42). Fowler has pointed out this evidence in favor of the Cuthbertson arrangement.

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[1] Goldstein, *Phys. Zeitschr.*, 6, 14, 1905.

The fact that apparently the entire band is increased in intensity may point to a further relation, not included in the Cuthbertson. It would be very interesting to photograph this spectrum under high dispersion and to note whether *all* the lines of a band were intensified, or only those belonging in series.

Angerer[2] has made an exhaustive study of the First Deslandres' Group at low temperature. I have made no critical study of his results, and cannot well do so until I have my own measurements completed. Several points, however, are worth noting.

At low temperature the heads of a band are far more intense, relative to the rest of the band, than at ordinary temperature. This is especially true of the III heads which, at high temperature, escape detection in many bands—not having been measured at all by von der Helm. But they are particularly strong at low temperature. This would point to an independence between the series lying within the heads of the bands, and other series.

At low temperature the entire spectrum is relatively much fainter than at room temperature. Aside from two small groups of lines in the green, the only exceptions to this statement are the first heads of the three bands λ 6623, λ 6070, and λ 5593 ($n=51$; $p=46$, 47, and 48). The second of these is even more intense at low temperature, while the other two are fully as intense. Here again we have evidence in favor of the Cuthbertson arrangement.

There is one additional fact pointing to a general relationship between the heads of all the bands. The frequency difference of the rough position of the I and IV heads is a constant for all bands from λ 5100 to λ 9100, although the length of the bands more than doubles within this range. The maximum variation of the difference is 7 units (from $v=68$ to 61). The frequency difference of the I and II heads, except in the *f* group, is also practically constant. I cannot recall having previously seen this fact explicitly stated.

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[1] Fowler, *Proc. Roy. Soc.*, 85 A, 377, 1911.

[2] *Ann. d. Phys.*, 32, 549, 1910.

This relation of the heads is what we should expect if the bands were composed of a number of identical series of lines. It seems evident that all possible series have *very closely* the same spacing, but it is also certain that the spacing is *not* identical.

Sections II and III may be summarized in the statement that numerical relationships among the lines of the First Deslandres' Group favor the von der Helm method of grouping, while changes in the bands under varying physical conditions of the source all point to the Cuthbertson method as the significant one.

CONCLUSIONS

1. The First Deslandres' Group of the positive band spectrum of nitrogen consists really of two spectra, one composed of a large number of superimposed series of lines, the other quite irregular.
2. The similarity in the spacing of all series gives the banded appearance of the spectrum, the length of a band being the distance between two successive lines of each series.
3. The so-called "heads" of the bands are formed by groups of particularly heavy lines, accompanied by more or less continuous radiation.
4. It is possible to fit a greater number of lines into the simple series of the von der Helm arrangement of bands than into the more complex two-parameter formula indicated by the Cuthbertson arrangement. All physical changes in the spectrum, however, favor the latter arrangement.
5. Simple series of lines, running through one band group of the von der Helm arrangement, obey Deslandres' Law for at least the first few bands, but later show a large and systematic deviation from it.
6. The First and Second Progressions of the Cuthbertson arrangement fit approximately into a formula containing both

the second and third powers of the parameter, but will ***not*** fit the simpler second-power formula of Deslandres' Law.

7. The successive band groups have certain heads which approximately coincide, and these points of coincidence show regularities which enable the entire set of bands of the First Deslandres' Group to be arranged so as to indicate a definite plan for the group.

The experimental part of the investigation is the resolving, for the first time, of the 39 bands between λ 5000 and λ 6800 into about 6400 lines, and the measurement of a portion of these lines with an average error of 0.01 A or less.

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